Thermal conductivity of graphene in Corbino membrane geometry

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Local laser excitation and temperature readout from the intensity ratio of Stokes to anti-Stokes Raman scattering signals are employed to study the thermal properties of a large graphene membrane. The concluded value of the heat conductivity coefficient $\kappa \approx 600$ W/m·K is smaller than previously reported but still validates the conclusion that graphene is a very good thermal conductor.

Keywords: Graphene; Graphene membrane; Thermal conductivity; Raman scattering.

Systems of fewer than three dimensions are considered to be very efficient heat spreaders as their intrinsic thermal conductivity may eventually diverge for infinite specimens, following a power or logarithmic law for one- or two-dimensional systems, respectively[1]. This conjecture is now being confronted with experimentations on graphene - a single sheet of graphite, the closest archetype of a two-dimensional crystal and promising material for various applications[2]. Although conventional methods to extract thermal properties of solids are not easily applicable to a system of a single atomic monolayer, the heat conductivity of graphene flakes has been shown to be conveniently investigated using contactless methods of local laser excitation combined with micro-Raman scattering spectroscopy[3]. Carbon crystallites such as diamond and graphite are known as the exceptional heat conductors[4] and an efficient thermal conductivity has been also reported for graphene[3]. This conclusion calls, however, for confirmation because the experimental methods applied to draw it are not fully straightforward. A precise (contactless) temperature readout, accurate sample geometry and exact estimations of the absorbed laser power are among subtle issues which may significantly influence the apparent values of the extracted thermal conductivity coefficient.

In this paper we report on room temperature studies of thermal properties of a relatively large graphene membrane[5,6]. Our Corbino-like experimental configuration together with the direct temperature readout from the intensity ratio of Stokes to anti-Stokes Raman scattering signals largely simplifies the data analysis. The presented results are in overall agreement with the previous studies[3,7] but we argue that the extracted value of the 3D-equivalent thermal conductivity coefficient for graphene may not be as high as it has been reported so far.

A photograph of our sample, the graphene membrane, as seen through a x100 microscope objective is presented in the inset of Fig. 1. The membrane fully covers the

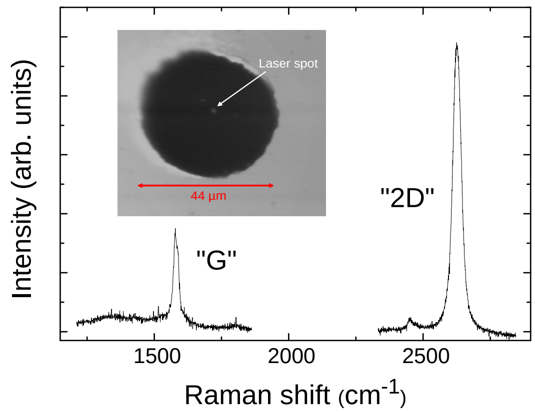

FIG. 1: The characteristic room temperature Raman scattering bands of the investigated graphene membrane, measured under 6.2 mW excitation of 632.8 nm He-Ne laser line focused on the middle of the membrane. Inset : Optical photograph of the graphene membrane. The diameter of the membrane is 44 μm and the white spot in the middle is the diffusion of the laser spot of 2μm diameter on the one atom thick graphene membrane.

44 μm diameter pinhole made in the 2 mm thick plate of copper. With the use of silver epoxy, the edges of the membrane (which extend outside the pinhole) are thermally short circuited to the copper plate which serves in our experiments as a room temperature heat sink. The suspended part of the membrane has a well defined circular geometry.

The groundwork of our experiments consists in using laser excitation to locally generate heat and measuring the Raman scattering spectra to extract the actual temperature of the membrane within the laser spot. The Raman scattering spectra shown in Fig. 1 reveal the characteristic "G" and "2D" bands[8,9] of graphene, measured on our membrane at room temperature when the laser spot is located at its center.

The local temperature of the membrane within the laser spot is derived from measurements of the Stokes and anti-Stokes Raman scattering signals corresponding to the low energy ($\hbar\omega_G$) phonon of graphene (G-band).

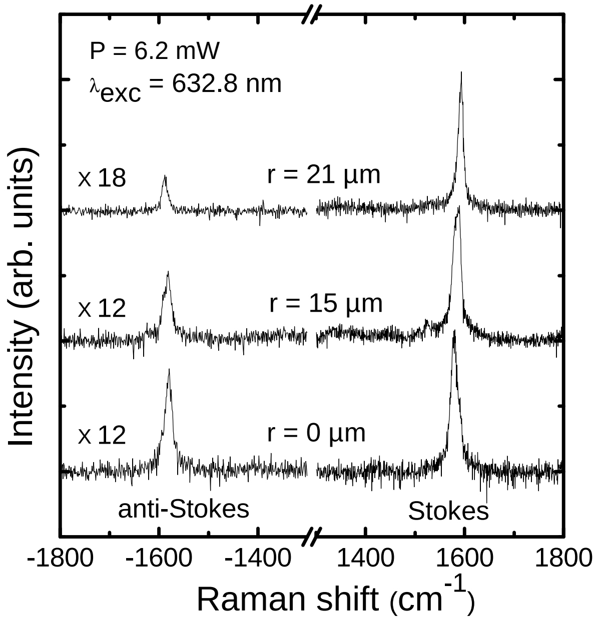

FIG. 2: Stokes and anti-Stokes Raman scattering spectra of the the G-band graphene membrane measured under 6.2 mW of laser excitation focused at different points on the membrane (at different distances r from the center of the membrane). Note the change in the ratio of Stokes to anti-Stokes signal, which reflects the drop of local temperature within the laser spot (2μm in diameter) when approaching the edge of the membrane (in thermal contact with a room temperature sink).

After a careful calibration of the response of the experimental set-up (with a black-body like tungsten radiation source and a two-color pyrometer), we read this temperature directly from the intensity ratio of the Stokes to anti-Stokes signals : $\frac{I(\omega_{exc}-\omega_G)}{I(\omega_{exc}+\omega_G)} = \exp(\frac{\hbar\omega_G}{k_B T})$. Such simple method of temperature readout is well justified when working with a single atomic layer. Reabsorption processes, which usually need to be taken into account for thick bulk samples, are negligible small in our case. Few examples of the measured Stokes and anti-Stokes components of the Raman scattering spectra of the G-band are shown in Fig. 2. As expected and seen in this figure, the laser excitation heats locally the membrane most efficiently when the laser spot is at the center of the membrane and significantly less when it is placed closer to the copper plate heat sink.

As further described in details, the temperature difference ΔT between the laser spot location and the membrane's edge is proportional to the absorbed laser power P and inversely proportional to the efficiency of the "heat spread": $\Delta T \sim P/\kappa d$, where κ is the 3D equivalent thermal conductivity coefficient and d is the thickness of the membrane. Knowing the proportionality factor, which depends on the geometry of the experimental configuration and can be calculated from the heat diffusion equation, we can extract the characteristic parameters of heat conductivity in graphene.

In the calculations we consider that the heat generation $q(\overrightarrow{r})$ in the membrane (disk of the radius R and thickness d) is due to a local, homogenous across the membrane but Gaussian-spread in plane, laser excitation: $q(\overrightarrow{r}) = \frac{P}{d\pi a^2}\exp(-|\overrightarrow{r}-\overrightarrow{r_0}|^2)/a^2)$. Here, $a = 1$ μm corresponds to the estimated radius of the laser spot on the sample, $P = d \cdot \int q(\overrightarrow{r}) d^2\overrightarrow{r}$ is the total absorbed laser power and $\overrightarrow{r}$ is the vector of the in plane polar coordinates which we center in the middle of the membrane. The temperature distribution in the membrane plane $T(\overrightarrow{r})$, and in particular its measured value at the location of the laser spot $T(\overrightarrow{r_0})$ is ruled by the steady state form of the heat diffusion equation:

$$\kappa \cdot \bigtriangledown^2 T(\overrightarrow{r}) + q(\overrightarrow{r}) = 0 \tag{1}$$

which after introducing the dimensionless variable $\overrightarrow{\rho} = \overrightarrow{r}/a$ takes here the following form :

$$\bigtriangledown^2 T(\overrightarrow{\rho}) + \frac{P}{\kappa\pi d}\exp(-|\overrightarrow{\rho}-\overrightarrow{\rho_0}|^2) = 0 \tag{2}$$

With fixed geometrical factors (R, a, $\overrightarrow{\rho_0}$) and under appropriate boundary conditions (room temperature at the edge of the membrane), the solution of equation (2) depends on a single parameter $\alpha = P/\kappa d\pi$. Conversely, the measure of temperature at any point of the membrane, and in particular at the location of the laser spot, allows us to determine α, and also to extract the entire temperature distribution in the membrane.

Equation (2) can be readily solved when the laser excitation is focused at the center of the membrane. The solution of our heat diffusion equation has a circular symmetry ($T(\overrightarrow{r}) = T(r)$) and takes the following form :

$$T(0) - T(\rho) = \frac{\alpha}{2}\int_0^\rho \frac{1-\exp(-x^2)}{x}dx =$$
$$= \frac{\alpha}{2}(\ln\rho - \frac{1}{2}Ei(-\rho^2) + \frac{\gamma}{2}) \approx \frac{\alpha}{2}(\ln\rho + \frac{\gamma}{2})$$

where Ei(x) denotes the exponential integral function, $\gamma = 0.5772$ is the Euler's constant and the approximation is well satisfied if $\rho > 1$.

In the experiment, the edges of the membrane are kept at ambient condition $T(\Lambda) = T_{edge} = 295$ K and Λ=R/a = 22. Thus $T(0) - T_{edge} \cong 1.689\alpha$. Under a 6.2 mW laser excitation, we obtain T(0)=660 K at the laser spot in the middle of the membrane and immediately obtain $\alpha = 216$ K.

The parameter α can also be extracted for an arbitrary experimental geometry (laser spot out of the center of the membrane) but then numerical solutions of the heat flow equation are required. This has been done using finite elements computations. As shown in Fig. 3, the measured local temperature within the laser spot located now at different positions with respect to the center of the membrane is well reproduced by the simulations assuming $\alpha = 214.4$ K. This value is not far from the one derived previously from a single measurement with the laser placed at the center of the membrane.

After evaluating α we can now extract the thermal conductivity coefficients of graphene but this requires an

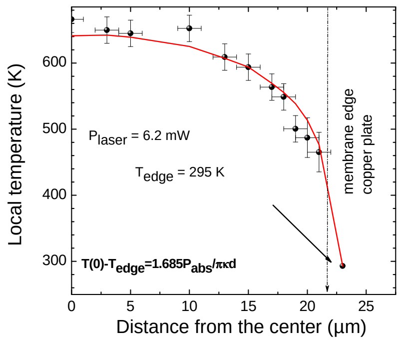

FIG. 3: Lattice temperature as deduced from the intensity ratio of Stokes and anti-Stokes signals of the graphene G-band raman scattering signals, (black dots), measured at room temperature with a laser power of 6.2 mW focused down to 2 μm diameter spot. The data point on the copper plate is fixed at T=295 K. The solid red line is the solution of the temperature profile obtained by finite elements simulation with $\alpha = 214.4$ K.

estimation of both the fraction of the laser power absorbed by the sample and of the thickness of the membrane. In our analysis, we assume a single laser pass through the membrane, which is justified in our experiment because the substrate below the membrane has been completely removed, preventing any parasitic back reflections. It has been demonstrated and confirmed by different studies[5,10,11] that the absorption of light in the visible range of energy in a graphene monolayer is determined only by fundamental constants, and is equal to $\pi e^2/(\hbar c 4\pi\epsilon_0) = \pi\alpha \approx 2.3\%$, where α is the fine structure constant. It follows from these studies that 2.3% of the total laser power (6.2 mW) is absorbed by the membrane. Hence, if $\alpha = 214.4$ K, the "two-dimensional" thermal coefficient of graphene is $\kappa \cdot d = 2.117 \cdot 10^{-7}$ W/K. Assuming $d = 0.335$ nm, corresponding to the inter layer distance in graphite, a 3D equivalent value κ=632 W/m·K is obtained.

This value of κ is by a factor 5 to 8 smaller than the one reported previously[3] but nevertheless indicates that heat spreading in graphene is as efficient as it is in graphite[12], the latter considered as an exceptional heat conductor. The difference between the present and previous estimations of α for graphene is mainly due to different assumptions regarding the absorbance of graphene. Our assumption of 2.3% of the absorbed laser power follows the results of very recent and precise transmission and reflectivity studies of graphene (membranes or deposited on a substrate) and graphite[5,10,11], and seems to be more realistic as compared to 13% assumed previously[3]. (Supposing 13% of the absorbed laser power, we would conclude $\kappa \approx 3600$ W/m·K, in fair agreement with previous data). We also note that our direct readout of local temperature confirms the applicability of the method used by Balandin *et al.*[3] to measure this temperature, which relies on the power dependent shift of the G-band, which on its hand is attributed to a temperature dependent shift known from independent experiments. When exciting at the middle of our membrane with different laser powers, we find that the G band Raman shift follows a linear variation with increasing optical power $\omega_G(P) = \omega_G(0) - P \cdot 0.8 cm^{-1}/mW$, where $\omega_G(0) = 1589.7 cm^{-1}$ is the limit for a vanishing excitation power. Assuming that $\Delta\omega/\Delta T = -0.0016 cm^{-1}/K^{13}$, we conclude that an increase of 1 mW of the excitation power corresponds to an increase of 50 K of the lattice temperature. Thus at the 6.2 mW excitation: $T = 605$ K which is not far from $T = 660$ K measured from the intensity ratio of Stokes to anti-Stokes signals.

To conclude, we have used micro-Raman scattering experiments to study the room temperature heat conductivity of a large graphene membrane. We have deduced that graphene is a thermal conductor as good as graphite. The 3D equivalent thermal coefficient of graphene is $\kappa \approx 630$ W/m·K, i.e., somewhat smaller than the values previously reported[3]. The difference between the present and previous estimations of κ is mainly due to different assumptions regarding the efficiency of the graphene's optical absorbance.

I. METHODS

Free standing graphene membranes were prepared by the method previously reported[6]. In brief, large (¿¿ 100 μm in size) graphene crystals were deposited on top of a silicon wafer, which was spin coated with a 90nm thick layer of PMMA. Single layers were identified by optical microscopy. By employing a series of photolithography and electro-deposition steps, we deposited a 15 to 20 μm thick copper film on top of the wafer. The film contained an opening of 50 to 100 μm in diameter, which was aligned with the chosen graphene crystal so that graphene fully covered the aperture. We used acetone to dissolve PMMA and thus release the copper scaffold with graphene attached into the liquid. The samples were finally dried in a critical pint dryer to prevent the membrane rupturing due to surface tension. Silver epoxy was used to place the scaffold to a thick copper plate to allow easy handling and the reported measurements.

Raman scattering experiments have been carried out at room temperature using the 632.8 nm line of the He-Ne laser as the excitation source and a confocal micro-Raman set-up equipped with a x100 microscope objective which provides a lateral resolution of $\sim 2\mu$m (diameter of the laser spot on the membrane). An X-Y translation stage together with an imaging camera allowed us to place the laser spot on the membrane at a given location with a precision of 0.1 μm; the excitation power is measured at the sample location with a calibrated silicon photodiode.

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